

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-013398  
(43)Date of publication of application : 22.01.1993

(51)Int. Cl.

H01L 21/304  
B08B 3/08  
G02F 1/13  
H05K 3/26

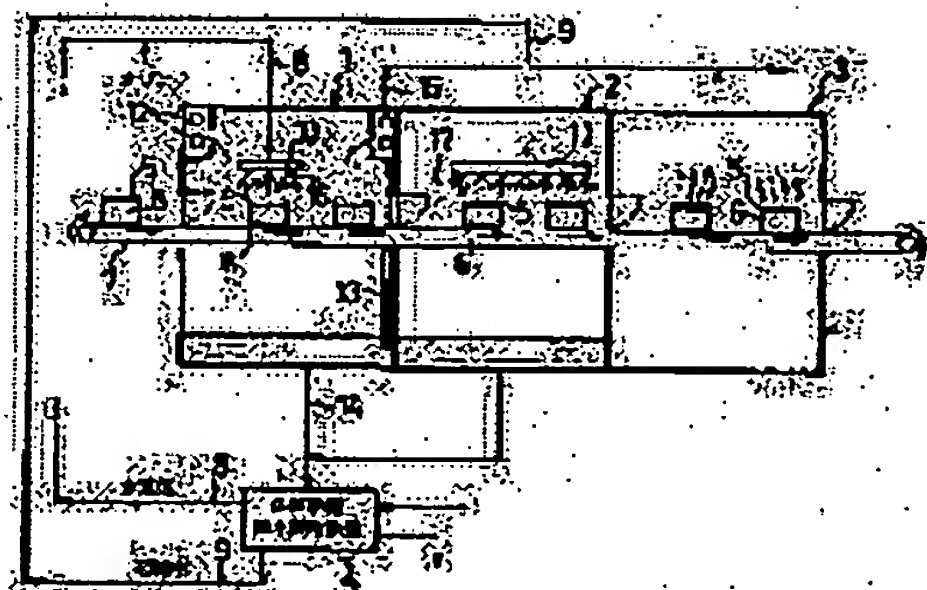
(21)Application number : 03-165387 (71)Applicant : HITACHI Zosen CORP  
(22)Date of filing : 05.07.1991 (72)Inventor : SAWADA HIDETAKA  
HIRANO TAKASHI  
MOMOSE SHOICHI  
INOUE SHIRO  
KOBAYASHI KAZUNORI  
SUEMATSU HIDEO

(54) CLEANING METHOD FOR SUBSTRATE

(57)Abstract:

PURPOSE: To make it possible to reduce the manufacturing cost of a device as there is no need to provide an organic contaminant cleaning process, to facilitate monitoring of the operation of the device and maintenance and management of the device and to make it possible to decompose many organic contaminants in a short time compared to a conventional cleaning of organic contaminants using ozone, which is performed at a temperature of about 20 to 30° C.

CONSTITUTION: A cleaning method of a substrate is characterized by that ozone is injected in clean steam obtained by a pure water manufacturing device 4 for multiple effect use to manufacture the mixed vapor of pure steam and the ozone, this mixed is made to jet through spray nozzles 16 in a vapor cleaning tank 1 to wash out contaminants adhered on the substrate 5 and at the same time, after filmy organic contaminants are made to decompose by the ozone, the substrate 5 is cleaned with high-purity water in a high-purity water cleaning tank 2.



LEGAL STATUS

[Date of request for examination] 14.10.1994  
[Date of sending the examiner's decision]

BEST AVAILABLE COPY

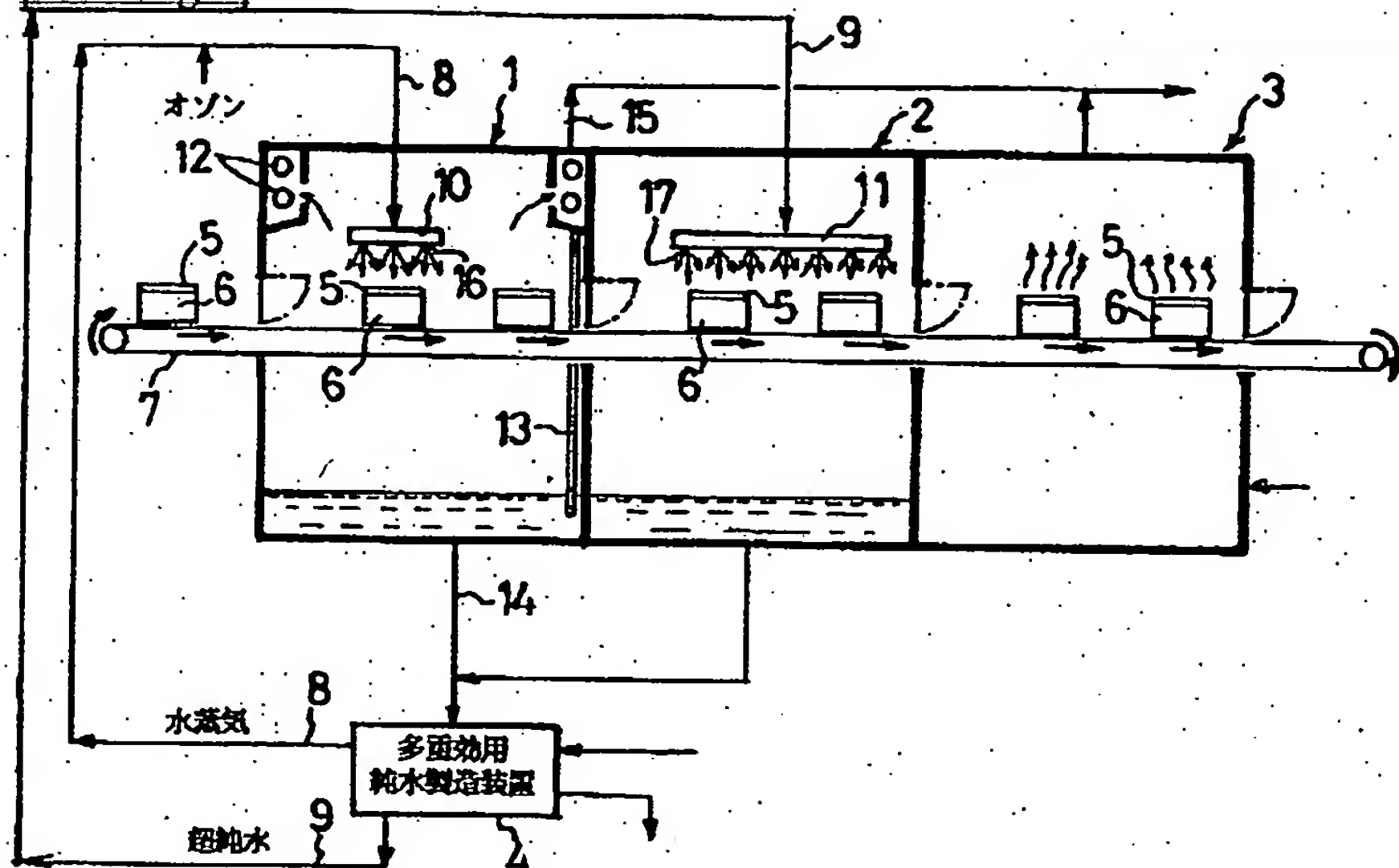
## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

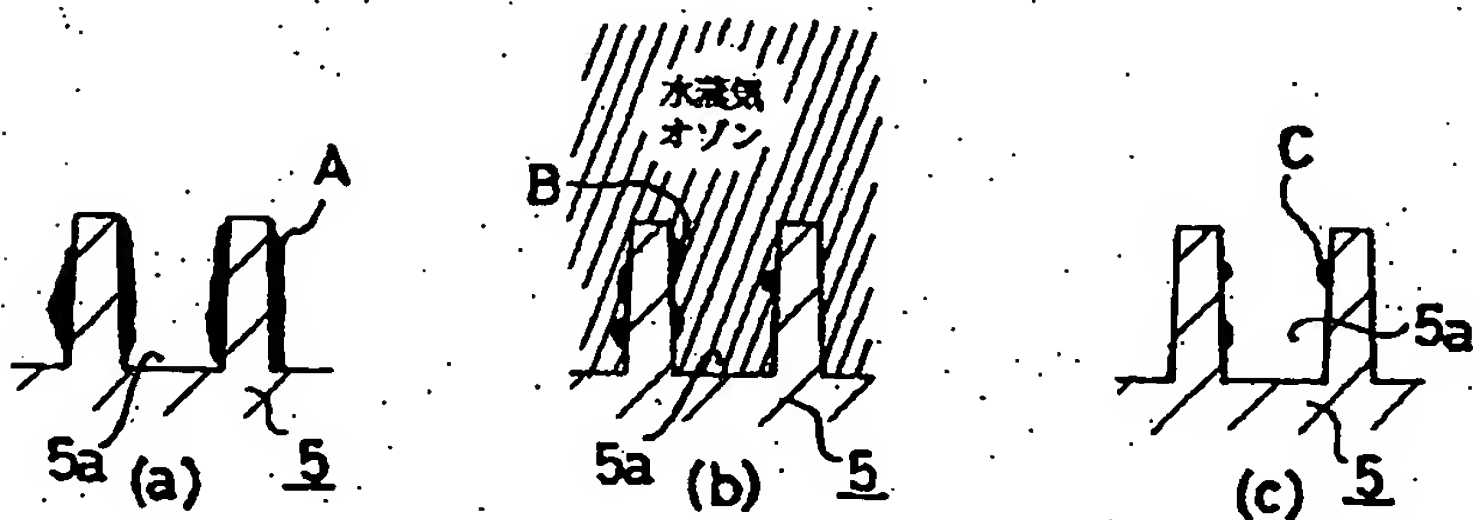
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

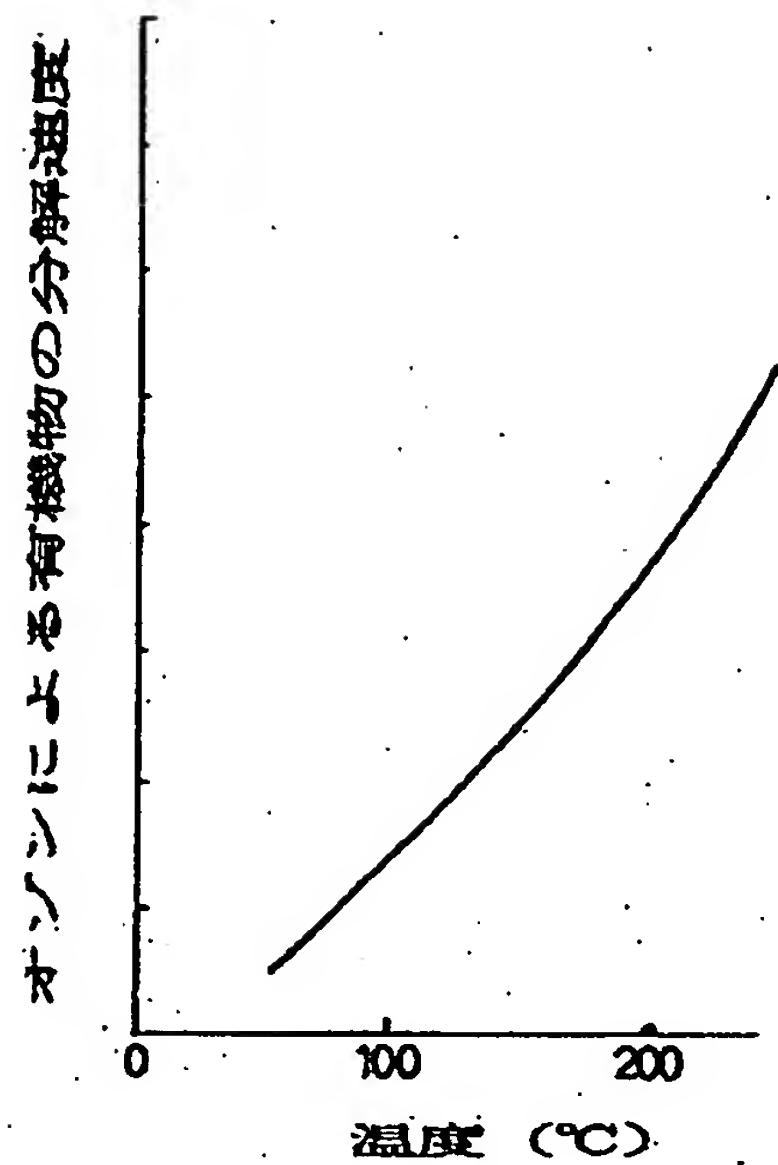
[Drawing 1]



[Drawing 2]



[Drawing 3]



---

[Translation done.]

(19) Japanese Patent Office (JP)  
(12) Official Gazette for Unexamined Patent Applications (A)

(11) Published Unexamined Patent No. H05(1993)-013398

(43) Publication Date: January 22, 1993

Number of Claims: 1 (total of 4 pages)

Examination Request Status: Not requested

Technical Indications Section:

(51)	International Class. <sup>5</sup>	Identification No.	JPO File No.	FI
	H 01 L 21/304	341 V	8831-4M	
	B 08 B 3/08	A	6704-3B	
	G 02 F 1/13	101	8806-2K	
	H 05 K 3/26		6736-4E	

(21) Application No.: H03-165387

(22) Application Date: July 5, 1991

(71) Applicant: 000005119

Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City, Osaka Prefecture

(72) Inventor: Hidetaka Sawada

Inside Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City

(72) Inventor: Takashi Hirano

Inside Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City

(72) Inventor: Shoichi Momose

Inside Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City

(and three others)

(74) Agent: Einosuke Kishimoto, Patent Attorney

Continued on the last page.

(54) Title of the Invention: Cleaning Method for Substrate

(57) Overview

<Purpose>

To present a cleaning method for substrates in which the following is made possible: reduction in the manufacturing cost of a device since there is no need to provide a process for cleaning away organic contaminants; facilitation of the monitoring and maintenance of a device; and decomposition of several organic contaminants within a short time frame when compared with conventional organic contaminant cleaning methods in which ozone is used at a temperature of approximately 20 – 30°C.

<Constitution>

A cleaning method for a substrate is characterized by the following: ozone is injected into a pure water vapor that is obtained through the use of a multi-effect water purification device (4), such that a mixed vapor of pure water vapor and ozone is created; this mixed vapor is sprayed out from spray nozzles (16) within a vapor cleaning tank (1) such that contaminants that have adhered to the substrate (5) can be washed away; at the same time, the filmy organic contaminants are decomposed by the ozone, after which the substrate is cleaned using ultra-pure water within an ultra-pure water cleaning tank (2).

[Drawing:]

4: Multi-effect water purification device

[left to right:]

Ozone

Water vapor

Ultra-pure water

## &lt;Claims&gt;

## &lt;Claim 1&gt;

A cleaning method for a substrate characterized by a mixed vapor of pure water vapor and ozone that is sprayed from spray nozzles in order to conduct cleaning, after which ultra-pure water is used for cleaning.

## &lt;Detailed Explanation of the Invention&gt;

## &lt;0001&gt;

## &lt;Industrial Field of Application&gt;

This invention pertains to a cleaning method for multiple types of substrates, particularly those that have undergone fine processing and are well-suited for cleaning, such as glass substrates used for liquid crystals, semiconductor substrates, etc.

## &lt;0002&gt;

The term "pure water vapor" used in these specifications means a clean form of vapor that is obtained through a process in which pure water or ultra-pure water is heated in order to create vapor as well as ultra-pure water.

## &lt;0003&gt;

## &lt;Prior Art&gt;

In a previous method for cleaning finely processed substrates as noted in Japanese Patent No. H01(1989)-189127, ultra-pure water is heated in order to produce vapor, to which the substrates are exposed, after which the substrates are cleaned using ultra-pure water.

## &lt;0004&gt;

## &lt;Problem to Be Solved by the Invention&gt;

With the aforementioned cleaning methods for substrates, vapor can penetrate the detailed areas of a substrate more easily than water can, and once the vapor is able to penetrate these finely processed areas of a substrate, ultra-pure water is used to increase the wettability of the substrate surface, which makes it possible to obtain a high level of cleaning effectiveness. However, in the case of organic contaminants, particularly filmy

organic contaminants that adhere to the finely processed areas of a substrate, it has been impossible to achieve a satisfactory level of cleaning effectiveness.

<0005>

Therefore, it has been necessary to provide a separate cleaning process for the removal of organic contaminants prior to the application of the cleaning process, such that ozone or an ammonia and hydrogen peroxide solution is used in which ammonia and hydrogen peroxide are mixed in pure water in order to use the process of oxide decomposition to remove the organic contaminants, particularly filmy organic contaminants that adhere to the finely processed areas of a substrate. This makes for a complicated cleaning system, increases the manufacturing cost of the devices used, and is troublesome from the standpoint of monitoring and maintaining such a device.

<0006>

The purpose of this invention is to present a cleaning method for substrates in which the following is made possible: reduction in the manufacturing cost of a device since there is no need to provide a process for cleaning away organic contaminants; facilitation of the monitoring and maintenance of a device; and decomposition of several organic contaminants within a short time frame when compared with conventional organic contaminant cleaning methods in which ozone is used at a temperature of approximately 20 – 30°C.

<0007>

<Means for Solving the Problem>

The cleaning method for a substrate as described in this invention is characterized by a mixed vapor of pure water vapor and ozone that is sprayed from spray nozzles in order to conduct cleaning, after which ultra-pure water is used for cleaning.

<0008>

<Operation>

By releasing a mixed vapor spray consisting of pure water vapor and ozone via the spray nozzles, the mixed vapor collides with the substrate, and this collision force works to wash away a portion of the contaminants that have adhered to the substrate surface, and the resulting fine atomization that occurs causes a



portion of the contaminants to be disbursed. Then, once the pure water vapor is able to penetrate the finely processed areas of the substrate, a post-process is applied in which ultra-pure water is used to increase the wettability of the substrate surface. At the same time, the ozone causes oxide decomposition to occur, which cleans away the filmy organic contaminants that have adhered to the finely processed areas of the substrate. The higher the temperature, the greater the oxide decomposition effect from the ozone, and since the pure water vapor heats the substrate, the ozone provides an increased oxide decomposition effect with respect to the organic contaminants.

<0009>

Subsequently, once the ultra-pure water is used to provide additional cleaning, the increased wettability of the substrate surface that follows the finely processed areas of the substrate as a result of the penetration of pure water vapor allows the ultra-pure water to also penetrate the finely processed areas of the substrate so that residual inorganic contaminants can also be washed away from the substrate, resulting in a substrate with a very high degree of cleanliness.

<0010>

<Embodiments>

In the following explanation, drawings are used as a reference in order to provide an embodiment of this invention.

<0011>

Figure 1 shows a substrate cleaning device that is equipped with the following: a vapor cleaning tank (1), an ultra-pure water cleaning tank (2), a drying chamber (3), a multi-effect water purification device (4), a mount (6) for the substrate (5) that is to undergo cleaning, and a conveyor (7).

<0012>

The multi-effect water purification device (4) consists of a device for the pre-treatment of tap water, a multi-effect distillation device for the primary pure water system, and a multi-effect distillation device for the secondary pure water system. The multi-effect distillation device for the primary pure water system provides primary pure water and primary pure water vapor from the tap water that has been sent through the pre-



treatment device. The multi-effect distillation device for the secondary pure water system provides secondary pure water vapor with a level of cleanliness equal to the ultra-pure water, and this is made possible through the delivery of the primary pure water and the heating of the primary pure water vapor. This secondary pure water vapor is then condensed to form the secondary pure water, namely the ultra-pure water.

<0013>

A portion of the secondary pure water vapor obtained from the multi-effect water purification device (4) is ejected in its vapor form and sent through a vapor pipe (8), at which point a clean form of ozone is injected to form a mixed vapor within the vapor cleaning tank (1) that is composed of pure water vapor and ozone to be used in the cleaning of the substrates. This mixed vapor passes through the vapor pipe (8) and is sent to the distribution pipe (10) where it is sprayed onto the substrate (5) from the multiple spray nozzles (16) installed within the distribution pipe (10).

<0014>

The ultra-pure water obtained from the multi-effect water purification device (4) is sent to the ultra-pure water cleaning tank (2) via the water pipe (9) where it is used in the cleaning of the substrates. The ultra-pure water passes through the water pipe (9) and is sent to the distribution pipe (11) where it is sprayed onto the substrate (5) from the multiple spray nozzles (17) installed within the distribution pipe (11).

<0015>

In this embodiment, the temperature of the pure water vapor is 105°C, the specific resistance of the ultra-pure water is 18.0 MΩ/cm, and the temperature of the ultra-pure water is 80°C. The operations within the substrate cleaning spaces of the vapor cleaning tank (1) and the ultra-pure water cleaning tank (2) are conducted under atmospheric pressure conditions.

<0016>

In the following example, Figure 2 is used as a reference with regard to the process in which a semiconductor substrate (5) is cleaned which contains a finely processed trench (5a).

(3)

<0017>

The drawing (see Figure 2) shows contaminants (A) that have adhered to the wall of the trench (5a) within the semiconductor substrate (5). The mixed vapor containing pure water vapor and ozone that has been sprayed onto the substrate (5) from the spray nozzles (16) located along the distribution pipe (10) within the vapor cleaning tank (1) collides with the substrate (5), at which time the collision force washes away a portion of the contaminants (A) that have adhered to the wall of the trench (5a), and the resulting fine atomization (B) that occurs causes a portion of the contaminants to be disbursed (see Figure 2b). Then, the pure water vapor penetrates the inside of the trench (5a) within the substrate (5), and the post-process is conducted in which ultra-pure water is used to increase the wettability of the surface. At the same time, the temperature of the substrate (5) is increased to nearly 105°C, and the ozone causes oxide decomposition to occur, in which case the filmy organic contaminants that have adhered to the wall of the trench (5a) are decomposed into carbon dioxide and water. As shown in Figure 3, the speed at which the ozone decomposes the organic matter increases as the temperature rises, and therefore it is possible to decompose a large number of organic contaminants within a short time frame when compared with conventional methods in which organic contaminants are cleaned away using ozone at a temperature of approximately 20 – 30°C.

<0018>

As such, upon completion of the cleaning process in which the mixed vapor is applied, the majority of the contaminants (A) are removed, and only inorganic contaminants (C) remain, which are dispersed as a result of the fine atomization process (see Figure 2c).

<0019>

Next, the substrate (5) that has been cleaned according to the process in which the mixed vapor is applied is sent to the ultra-pure water cleaning tank (2) via the conveyor (7) in order to undergo the ultra-pure water cleaning process.

<0020>

Since the cleaning process in which the mixed vapor is applied causes an increase in the wettability of the trench (5a) wall surface due to the penetration of the pure water vapor, the ultra-pure water that is sprayed from the spray nozzles (17) along the distribution pipe (11) can easily penetrate the inside of the trench (5a) so that the main contaminants (B), which are in the form of inorganic matter remaining within the trench (5a) can be washed away, leaving a clean substrate (5). At this point, the ultra-pure water within the trench (5a) receives spray energy that causes a stirring action within the trench (5a). In addition, new ultra-pure water is delivered into the trench (5a) in a sequential fashion, making it possible to clean the substrate (5) with a high level of efficiency.

<0021>

Next, the substrate (5) that has been cleaned using the ultra-pure water is sent to the drying chamber (3) via the conveyor (7), and cold-blast drying is conducted within the drying chamber (3) using clean nitrogen gas.

<0022>

The pure water vapor within the mixed vapor after the substrate (5) has been cleaned is condensed for the most part along the outer surface of the cooling pipe (12) that is installed along the top of the cleaning tank (1) and through which cooling water flows. It then passes through a down pipe (13) to the bottom of the vapor cleaning tank (1), after which it passes through a drain pipe (14) that is installed onto the bottom of the vapor cleaning tank (1) and returns to the multi-effect water purification device (4) where it is reused. Note that the uncondensed portion of the pure water vapor as well as the ozone pass through the vent pipe (15) and are discharged to the outside of the vapor cleaning tank (1).

<0023>

<Effect of the Invention>

By applying the cleaning method for substrates described in this invention, it becomes unnecessary to provide a separate cleaning process for the removal of organic contaminants due to the following: by spraying a mixed vapor containing pure water vapor and ozone from spray nozzles onto the surface of a substrate, a portion of the contaminants that have adhered to the substrate surface can be washed away, and a portion can be dispersed as a result of a fine atomization process; this pure water vapor can penetrate the finely processed

portions of the substrate, and while a post-process is conducted in which ultra-pure water is used to increase the wettability of the substrate surface, the ozone causes oxide decomposition to occur, which cleans away the filmy organic contaminants that have adhered to the finely processed areas of the substrate. Accordingly, it becomes possible to reduce the manufacturing cost of the device as well as to facilitate the monitoring and maintenance of the device.

<0024>

Moreover, as the substrate is heated by the pure water vapor, the ozone provides an increased oxide decomposition effect with respect to the organic contaminants. Therefore, it is possible to decompose a large number of organic contaminants within a short time frame when compared with conventional methods in which organic contaminants are cleaned away using ozone at a temperature of approximately 20 – 30°C.

<Brief Description of the Drawings>

<Figure 1> A vertical cross-sectional diagram of the device described in the Embodiment of this invention.

<Figure 2> A cross-sectional diagram that illustrates the order of the processes in which cleaning is conducted using a mixed vapor containing pure water vapor and ozone.

<Figure 3> A graph that illustrates the relationship between temperature and the speed at which organic contaminants are decomposed using ozone.

<Explanation of Symbols>

- (1) Vapor cleaning tank
- (2) Ultra-pure water cleaning tank
- (4) Multi-effect water purification device
- (5) Substrate
- (8) Vapor pipe
- (9) Water pipe
- (10), (11) Distribution pipes
- (16), (17) Spray nozzles

<Figure 1>

[top to bottom:]

Ozone

Water vapor

Ultra-pure water

4: Multi-effect water purification device

<Figure 2>

Water vapor

Ozone

<Figure 3>

[y-axis:]

Decomposition speed of organic matter using ozone

[x-axis:]

Temperature (°C)

Continued from the front page:

(72) Inventor: Shiro Inoue  
Inside Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City

(72) Inventor: Kazunori Kiba  
Inside Hitachi Zosen Corp.  
5-3-28 Nishikujo, Konohana-ku  
Osaka City

(72) Inventor: Hideo Suematsu  
Inside Hitachi Zosen Corp.

5-3-28 Nishikujo, Konohana-ku  
Osaka City

-598-